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(54) **RADIATION-BARRIER MATERIAL CAPABLE OF SIMULTANEOUS SHIELDING AGAINST -g(g)-RAY, X-RAY AND NEUTRON BEAM.**

(57) A radiation-barrier material capable of simultaneous shielding against γ -ray, X-ray and neutron beam, comprising 100 parts by weight of at least one thermosetting resin material selected from the group consisting of phenol, epoxy, cresol, xylene, urea and unsaturated polyester resins and 50-2,000 parts by weight of at least one inorganic substance selected from the group consisting of Pb, W, Cr, Co, Cu, Fe, Mn, Mo, Ag, Ta, Cd, Dy, Eu, Gd, Au, In, Hg, Re, Sm and U and compounds of these elements, and giving a molding with a density of 2.0 or above.

EP 0 628 968 A1

[Technical Field]

This invention relates to a radiation shielding material for simultaneously shielding gamma-rays, X-rays and neutron rays. More particularly, it relates to a radiation shielding material for radiation facilities, for
 5 containers for storing and transporting radioactive wastes, nuclear fuels, radioisotope (RI) and the like, and for associated apparatuses and appliances.

[Background Art]

10 As to shielding of gamma-rays and X-rays among radiations, any materials do not make a great difference therebetween in a mass attenuation coefficient, and because a material having a high density has a large linear attenuation coefficient and it can be used in a less thickness as a shielding body, lead, iron, concrete, etc., have been generally used as shielding materials.

To shield neutron rays, there have been mainly used high-molecular materials such as polyethylene,
 15 paraffin, boron-mixed epoxy resins and materials containing large quantities of hydrogen such as water. Since concrete also contains hydrogen, it is used as a structural material additionally serving as a shield.

To shield the neutron rays, hydrogen is extremely important. Fast neutrons irradiated into a material will lose their energy due to elastic scattering with hydrogen atom therein and turn into thermal neutron rays, which are then captured by atomic nuclei of hydrogen and other elements. The thermal neutron rays are
 20 more easily captured by atomic nuclei having greater thermal neutron capture cross section. But there are some cases where secondary gamma-rays are emitted in this case, and therefore, shield against the secondary gamma-rays must be taken into consideration when neutron rays are attempted to be shielded.

Accordingly, in a case where neutron rays are shielded or neutron rays and gamma- and X-rays are simultaneously shielded, a material such as polyethylene, paraffin or water for shielding neutron rays, and a
 25 material such as lead or iron for shielding gamma-rays have heretofore been used in combination by laminating these two kinds of materials. Therefore, radiation facilities, containers for storing and transporting radioactive wastes, nuclear fuels, RIs and the like, and associated apparatuses and appliances, which are particularly accompanied with the emission of neutron rays, are constructed or fabricated from concrete, lead or iron each having a high density, and, furthermore, a shielding body is prepared from polyethylene,
 30 paraffin or water which is quite different as a shielding material from the above concrete etc., or a concrete structure alone is used as the shielding body.

When a shielding body is solely constructed by concrete, the wall thickness must be considerably great because the shielding capacity of concrete is not sufficiently high, thereby to make the available area of the facility small. Further, the concrete structure is likely to absorb radioactively contaminated water due to its
 35 water absorptivity, and, therefore, a water-proofing coating or top coat of a polymer concrete must be formed on the concrete structure. This results in a drastic increase of shielding cost.

When concrete, iron, lead and the like are combined with polyethylene, paraffin and the like, bondabilities therebetween are low thereby to make difficult the working of these materials and the production of shields therefrom. Therefore, a special process for producing such shields must be employed
 40 In this case. Further, because the coefficients of thermal expansion are remarkably different between these two kinds of materials, cracks, warpage, separation and the like occur to these materials depending on ambient temperatures. Accordingly, considerable care must be taken of temperature control after construction or production of the shields. In addition, since polyethylene and paraffin can be molten at a relatively low temperature and paraffin is easily ignitable, close attention must be paid to heat- and fire-resistance.
 45 Eventually, the shielding facility or product made under the above circumstances will become an extremely expensive one. When water is used for shielding neutron rays, sites where water is used and methods of using water are limited because it is a liquid.

It is an object of the present invention to provide an economical, new type radiation shielding material which simultaneously shields neutron rays and gamma- and X-rays thereby to eliminate the necessity for a
 50 double structure causing the problems described above, which has a sufficient strength, an excellent moldability and machinability, and which is excellent in heat resistance, hydrophobicity and chemical resistance.

Conventionally, it has been customary to classify radiation shielding materials into those for use in shielding gamma- and X-rays and those for use in shielding neutron rays. Materials having large densities
 55 are effective as shielding materials for gamma- and X-rays, whereas materials containing large quantities of hydrogen have great effects for neutron rays and, accordingly, materials having lower densities are conceptually believed effective. Therefore, both types of these shielding materials are contradictory in use to each other and they are not believed to be used together.

Further, it has been believed that the hydrogen content (wt.%) of a composition comprising a high density inorganic material and a synthetic resin remarkably decreases as compared with that of a molded article made of such a resin alone as used as the matrix in said composition, and the neutron shielding capacity of the composition decreases accordingly.

[Disclosure of the Invention]

The present inventors have paid their close attention to the fact that what is important for shielding neutron rays is not a mere hydrogen content (wt.%) but the number of hydrogen atoms per unit volume (hydrogen atom density) of a shield used, and have found out that a composition obtained by mixing a high-density inorganic material with a thermosetting resin material containing a large quantity of hydrogen does not exhibit a remarkable decrease in hydrogen atom density as compared with such a resin alone as used as the matrix in said composition, and has performance rather superior to the matrix resin alone in respect of the shielding effect on neutron rays. The present invention has been made on the basis of this finding.

According to the present invention, there is provided a radiation shielding material capable of simultaneously shielding gamma- and X-rays, and neutron rays, which comprises 50 to 2,000 parts by weight of at least one inorganic material selected from the group consisting of Pb, W, Cr, Co, Cu, Fe, Mn, Mo, Ag, Ta, Cd, Dy, Eu, Gd, Au, In, Hg, Re, Sm, U and compounds thereof, based on 100 parts by weight of at least one thermosetting resin material selected from the group consisting of a phenol resin, an epoxy resin, a cresol resin, a xylene resin, a urea resin and an unsaturated polyester, and wherein the density of a molded article of said inorganic material-containing resin is at least 2.0.

First, a thermosetting resin which contains a large quantity of hydrogen and is highly resistant to heat, is a preferable one for use in the radiation shielding material according to the present invention. The thermosetting resins which may be used in the present invention include a phenol resin, an epoxy resin, a cresol resin, a xylene resin, an urea resin, an unsaturated polyester and the like. These thermosetting resins may be used singly or jointly by mixing these resins. The thermosetting resin has a sufficient strength, excellent moldability and machinability, and has a relatively high heat resistance. Depending on the resin selected, it can be used at temperatures above 150 °C. The range of the molecular weight of the thermosetting resin used in the present invention and the degree of polymerization thereof are not particularly limited.

The higher the density of an inorganic material is, the greater the shielding effect thereof on gamma- and X-rays is, and an element having a greater thermal neutron capture cross section or a material containing such an element in a larger amount has a greater shielding effect on neutron rays. Accordingly, an inorganic material having a high density and containing a large amount of such an element or a combination of such materials can be used to produce a radiation shielding material having a further higher effect. The high-density inorganic material to be used for the present invention is at least one member selected from the group consisting of Pb, W, Cr, Co, Cu, Fe, Mn, Mo, Ag, Ta, Cd, Dy, Eu, Gd, Au, In, Hg, Re, Sn and U alone and compounds thereof, in the form of powder or pellet. These compounds include minerals such as iron ore, nickel ore and copper ore.

The amount of the inorganic materials added to the thermosetting resin is preferably within the range of from 50 to 2,000 parts by weight based on 100 parts by weight of the thermosetting resin. If the amount is less than 50 parts by weight, the shielding effect on gamma-rays and X-rays is inferior, and if it exceeds 2,000 parts by weight, the shielding effect on neutron rays decreases and at the same time, molded articles obtained are brittle and their mechanical strength decreases.

The highest shielding effect can be obtained by suitably determining a mixing ratio within the above mixing range depending on the intensity and characteristics of each radiation to effect shielding in the environment where various radiations such as neutron rays and gamma-rays co-exist. When the above mixture or composition is cured and molded, the resulting molded article must have a density of at least 2.0. If it has a density of less than 2.0, its shielding effect on gamma- and X-rays is inferior whereby simultaneous shielding of these different rays is made impossible. Since the density of concrete is generally from 2.0 to 2.2, the density of the molded article must be greater than the shielding capacity of concrete.

When powdery or granular inorganic material having a high density is kneaded with a thermosetting resin solution, there are some cases where a molded article having a sufficient density cannot be obtained due to inclusion of air in the kneaded mixture or due to the presence of a residual volatile material, which is used as a diluting agent of the resin, therein. To solve such a problem, it is effective for enhancing the density of the resulting molded article to employ defoam-kneading under a reduced pressure or in vacuum or to add an anti-foaming agent which reduces the surface tension of the mixture and permits easy escape of air bubbles from the mixture. The above procedure was confirmed to be also effective for improving the

shielding performance of the molded article on various radiations. A silicone or alcoholic defoaming (or anti-foaming) agent, for example, can be used in the present invention. The amount of defoaming agent added is generally preferably up to 1 wt.% of the total weight of the mixture.

It was further found out in the present invention that the thermosetting resin is mixed with the high-
 5 density inorganic material and further with a hydrogen-occluding alloy which has a relatively high dissociation temperature and can hold hydrogen therein up to a high temperature, thereby to further increase the resulting mixture in hydrogen atom density while allowing it to keep its high density. The hydrogen-occluding alloy is very effective for simultaneously shielding neutron rays, gamma-rays and X-rays, because it has a hydrogen atom density equally to polymer compounds such as the resin but has a higher density
 10 than the polymer compounds.

The hydrogen-occluding alloy can store hydrogen in the form of a metal hydride by reacting it with hydrogen gas. Although the hydrogen-occluding alloys such as Ti type, La (R) type, Mg type and Ca type ones are known, among which the Mg-type alloy which has a high hydrogen dissociation temperature at a normal pressure is believed to be the most suitable for the object of the present invention. The hydrogen-
 15 occluding alloys that can be used in the present invention include metal hydrides of Mg origin such as MgH_2 , Mg-Ni origin such as $Mg_2NiH_{4.2}$, Mg-Cu origin such as $MgCuH_{2.7}$, Mg-Ca origin such as $MgCaH_{3.72}$ and La-Mg origin such as $La_2Mg_{17}H_{17}$. The amount of hydrogen-occluding alloy added is preferably within the range of from 1 to 50 parts by weight based on 100 parts by weight of the thermosetting resin, in view of the cost of the resulting product and radiation shielding performance thereof.

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[Preferred Embodiment of the Invention]

The present invention will then be explained with reference to Examples, but the invention is in no way limited thereto.

25 The test for shielding performance was conducted by determining the thickness (1/10 value layer) of each test piece which reduces the dose equivalent rate of each radiation to 1/10, and making evaluation by using the 1/10 value layer. The test used ^{252}Cf as the neutron source and ^{60}Co as the gamma-ray source.

[Test 1]

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A liquid bis-phenol modified epoxy resin ("Epicon R-130A", a product of Dai-Nippon Ink & Chemical Co., Ltd.; curing agent "Epicon R-130BW", a product of Dai-Nippon Ink & Chemical Co., Ltd.) and a liquid phenol resin ("Resitop PL-4558", a product of Gun-ei Kagaku Kogyo K.K., soluble in methanol) as the thermosetting resins, were selectively mixed with the high-density inorganic materials which are metal lead
 35 powder, lead(II) oxide (specific gravity = 9.53), powder of Wolframite (specific gravity = approx. 7.16) that is a mineral containing tungsten(VI) oxide as its principal component, and iron pellets (specific gravity = 7.85) in accordance with the mixing ratios shown in Table 1, respectively, thereby to produce mixtures. Degassing-kneading and addition of 1 wt.% of a defoaming agent ("KS-603", a product of Shinetsu Kagaku Kogyo K.K.) based on the mixture of the resin and the inorganic materials except the iron pellets) were
 40 effected on the mixtures. The mixtures thus obtained were each poured into a mold, cured and molded into a molded article having a size of 60 x 60 x 2 cm. Each of the molded articles was measured for its density, shielding performance, hydrogen content (wt.%) and hydrogen atom density. For comparison, similar tests were carried out on an epoxy resin alone (Test No. 1), polyethylene (a low density polyethylene, a product of Sumitomo Bakelite K.K., No. 15), concrete (No. 16) and carbon steel (SS41, No.
 45 17). The results are shown in Table 1.

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T a b l e 1

| No. | component mixing ratio (parts by weight) | | | | | density (g/cm ³) | hydrogen content (wt.%) | hydrogen atom density (x10 ²² /ml) | 1/10 value layer (cm) | |
|-----|--|-----------------|----------------|------------|---------------|---------------------------------|--|--|-----------------------|-----------------------|
| | epoxy resin | phenol resin | lead powder | Wolframite | lead oxide | iron pellet | | | 252-Cf neutron | 60-Co gamma ray |
| 1 | 100 | 0 | 0 | 0 | 0 | 0 | 1.35 | 8.04 | 15.8 | 93.0 |
| 2 | 100 | 0 | 50 | 0 | 0 | 0 | 2.05 | 5.38 | 15.6 | 22.5 |
| 3 | 100 | 0 | 0 | 100 | 0 | 0 | 2.23 | 4.05 | 15.4 | 20.0 |
| 4 | 100 | 0 | 0 | 0 | 100 | 0 | 2.33 | 4.05 | 15.2 | 18.2 |
| 5 | 100 | 0 | 0 | 150 | 0 | 0 | 2.53 | 3.25 | 16.0 | 17.2 |
| 6 | 100 | 0 | 0 | 0 | 150 | 0 | 2.74 | 3.25 | 15.8 | 15.7 |
| 7 | 100 | 0 | 0 | 115 | 115 | 0 | 3.13 | 2.46 | 16.1 | 19.8 |
| 8 | 100 | 0 | 0 | 200 | 200 | 0 | 3.81 | 1.66 | 16.3 | 11.8 |
| 9 | 50 | 50 | 0 | 115 | 115 | 0 | 3.10 | 2.33 | 16.3 | 14.1 |
| 10 | 100 | 0 | 0 | 115 | 115 | 1200 | 5.64 | 0.54 | 27.3 | 8.1 |
| 11 | 100 | 0 | 0 | 200 | 200 | 1500 | 5.89 | 0.40 | 31.5 | 7.8 |
| 12 | 100 | 0 | 0 | 150 | 150 | 2000 | impossible to produce testpieces due to its britleness | | | |
| 13 | 50 | 50 | 0 | 115 | 115 | 1200 | 5.52 | 0.50 | 28.9 | 8.3 |
| 14 | 50 | 50 | 0 | 150 | 150 | 2000 | impossible to produce testpieces due to its britleness | | | |
| 15 | polyethylene | | | | | | 0.92 | 14.40 | 13.0 | 44.5 |
| 16 | concrete | | | | | | 2.10 | 1.10 | 31.0 | 26.0 |
| 17 | carbon steel (SS41) | | | | | | 7.85 | - | 98.6 | 7.2 |

It is obvious from Table 1, the test pieces of Nos. 2 to 9 which are Examples have neutron shielding capability equal to, or higher than, that of the epoxy resin alone of No. 1 which is Comparative Example, have improved gamma-ray shielding capability due to the increase of their densities, and also have high performances of shielding gamma-rays and X-rays as well as neutron rays.

It is also apparent from Table 1 that the test pieces of Nos. 10, 11 and 13 which are Examples have neutron-ray shielding capacity equal to, or higher than, that of concrete of No. 16 as a Comparative

Example, have excellent gamma-ray shielding capability approximate to that of the carbon steel (SS41) of No. 17, and have high gamma- and X-ray shielding performances and neutron-ray shielding performance.

When the gamma-ray shielding performance of the products of any Examples and neutron-ray shielding performances thereof are integrally taken into consideration, said products obviously have superiority to those of any Comparative Examples, and gamma- and X-ray shielding performances as well as neutron-ray shielding performance can be arbitrarily set by changing the mixing ratios for the component materials for products to be obtained. Accordingly, there can be obtained a shielding material which is the most effective for use under particular existing circumstances.

From the fact that it was impossible to produce a molded shielding material (test piece) from the component materials of Nos. 12 and 14 since a shielding material to be obtained was so brittle and that the shielding material (test piece) of No. 11 had a lower shielding performance or capacity than the concrete, it is understood that when the high-density inorganic material is used in an amount by weight of more than 2,000 parts per 100 parts by weight of the thermosetting resin, the resulting shielding material (test piece) will neither exhibit sufficient shielding effects on neutron rays nor produce therefrom a molded article having a sufficient strength.

[Test 2]

For comparison, there were prepared test pieces each having the same composition as that of No. 7 in Test 1, one being prepared without addition of a defoaming or anti-foaming agent thereto, another without degassing-kneading treatments and still another without any of such addition and treatments. These test pieces so prepared were each tested for density and shielding performance in comparison with the test piece of No. 7. The defoaming agent was a silicone-based one which was added to a mixture of the resin and inorganic materials in an amount of 1 wt.% of the mixture, and the degassing-kneading was carried out at a reduced pressure. The test results are as shown in Table 2.

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T a b l e 2

| No. | component mixing ratio (parts by weight) | | | addition of anti- foaming agent | degassing- kneading | density (g/cm ³) | hydrogen atom density (x10 ²² /ml) | 1/10 value layer (cm) | |
|-----|---|------------|---------------|--|------------------------|---------------------------------|--|-----------------------|-----------------------|
| | epoxy resin | Wolframite | lead oxide | | | | | 252-Cf neutron | 60-Co gamma ray |
| 7 | 100 | 115 | 115 | ○ | ○ | 3.13 | 4.597 | 16.1 | 13.8 |
| 18 | 100 | 115 | 115 | x | ○ | 3.09 | 4.448 | 17.1 | 14.9 |
| 19 | 100 | 115 | 115 | ○ | x | 3.08 | 4.523 | 17.1 | 14.9 |
| 20 | 100 | 115 | 115 | x | x | 2.89 | 4.150 | 17.5 | 15.6 |

It is apparent from Table 2 that when a high-density shielding material is to be produced, the addition of the anti-foaming agent and treatments of degassing-kneading will have considerable favorable effects on the shielding performance of the resulting product, to say nothing of increasing the density thereof.

[Test 3]

The procedure for preparing the test piece of No. 5 was followed except that the Wolframite was reduced in amount and, instead, a hydrogen-occluding Mg-Ni alloy ($\text{Mg}_2\text{NiH}_{4.2}$) was used as one of the component materials, thereby to obtain a new test piece (No. 21) comparison. In addition, the procedure for preparing the test piece of No. 6 was followed except the lead oxide was reduced in amount and, instead, the same Mg-Ni alloy as above was used as one of the component materials, thereby to obtain a new test piece (No. 22). These new test pieces so obtained were each tested for density, hydrogen atom density and shielding performance, in comparison with those of No. 5 and 6, respectively. The Mg-Ni type hydrogen-occluding alloy can hold hydrogen up to a high temperature of 300 °C or above under a normal state. The component materials for the test pieces Nos. 21 and 22 were also subjected to degassing-kneading and incorporated with the foaming agent. The results are shown in Table 3.

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T a b l e 3

| No. | component mixing ratio (parts by weight) | | | | density (g/cm ³) | hydrogen atom density ($\times 10^{22}/\text{ml}$) | 1/10 value layer (cm) | |
|-----|---|------------|---------------|---------------------------------|---------------------------------|---|-----------------------|-----------------------|
| | epoxy resin | Wolframite | lead oxide | hydrogen- occluding alloy | | | 252-Cf neutron | 60-Co gamma ray |
| 5 | 100 | 150 | 0 | 0 | 2.53 | 4.917 | 16.0 | 17.2 |
| 21 | 100 | 125 | 0 | 25 | 2.50 | 5.391 | 15.7 | 17.2 |
| 6 | 100 | 0 | 150 | 0 | 2.74 | 5.326 | 15.8 | 15.7 |
| 22 | 100 | 0 | 125 | 25 | 2.69 | 5.801 | 15.3 | 15.7 |

It is apparent from Table 3 that the test pieces of Nos. 21 and 22 obtained by including the hydrogen-occluding alloy as one of the component materials as mentioned above have gamma-ray shielding performances equivalent to those of the test pieces of Nos. 5 and 6 not containing the hydrogen-occluding alloy, respectively, but they have higher neutron-ray shielding performances than those of the test pieces of Nos. 5 and 6, respectively. Therefore, it is apparent that the former are superior to the latter.

[Effect of the Invention]

Since the radiation shielding materials according to the present invention have far higher simultaneous shielding capability against gamma-rays, X-rays and neutron rays than conventional laminate type materials and concrete, the former can be made compact in size. The optimum shielding material can be designed by appropriately changing the mixing ratio of the component or raw materials. Further, a shielding material having mechanical strength and heat resistance sufficient for use can be produced by selecting the kinds of thermosetting resin and high-density inorganic materials and the production method for the shielding material. Technology for molding the thermosetting resin as the matrix has been already established in various fields, and the shielding materials of the present invention can be produced by utilizing such technology and equipment. Accordingly, and, thus, it is possible to stably provide the shielding materials at a lower cost.

Claims

1. A radiation shielding material for gamma-rays, X-rays and neutron rays which comprises 100 parts by weight of at least one thermosetting resin material selected from the group consisting of a phenol resin, an epoxy resin, a cresol resin, a xylene resin, a urea resin and an unsaturated polyester, and 50 to 2,000 parts by weight of at least one inorganic material selected from the group consisting of Pb, W, Cr, Co, Cu, Fe, Mn, Mo, Ag, Ta, Cd, Dy, Eu, Gd, Au, In, Hg, Re, Sm, U and compounds thereof, the density of a molded article to be obtained from the radiation shielding material being at least 2.0.
2. A radiation shielding material according to claim 1, wherein a hydrogen-occluding alloy is further contained.
3. A radiation shielding material according to claim 1, wherein a defoaming agent is further contained.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP93/01799

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁵ G21F1/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁵ G21F1/00-1/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1926 - 1993

Kokai Jitsuyo Shinan Koho 1971 - 1993

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| Y | JP, A, 59-163597 (NEC Corp.), September 14, 1984 (14. 09. 84), Line 5, column 1 to line 1, column 2, (Family: none) | 1 |
| Y | JP, A, 63-293498 (Mitsubishi Cable Industries, Ltd.), November 30, 1988 (30. 11. 88), Lines 5 to 18, column 1, (Family: none) | 1 |
| Y | JP, A, 1-253696 (Asuk K.K.), October 9, 1989 (09. 10. 89), Line 5, column 1 to line 14, column 3, (Family: none) | 1 |



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

February 14, 1994 (14. 02. 94)

Date of mailing of the international search report

March 8, 1994 (08. 03. 94)

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